

COKE OVEN EMISSIONS*

First Listed in the *Second Annual Report on Carcinogens*

CARCINOGENICITY

Coke oven emissions are *known to be human carcinogens* based on sufficient evidence of carcinogenicity in humans (IARC 1984, 1987). Epidemiologic studies have shown increased incidences of lung cancer in humans exposed to coke oven emissions. Mortality studies have demonstrated increases in lung and genitourinary system cancer among coke oven workers. An IARC Working Group also stated that there is limited evidence that such occupational exposures induce cancer of the kidney and that there is inadequate evidence for intestinal and pancreatic cancer (IARC 1984). EPA estimated that 1.5 to 16 lung cancer deaths per year are associated with exposure to coke oven emissions (Chem. Eng. News 1984).

An IARC Working Group reported that there is sufficient evidence of carcinogenicity of coke oven emissions in experimental animals (IARC 1984, 1987). When administered topically, coke oven emissions induced skin carcinomas and papillomas in mice of both sexes. When administered by inhalation, coal tar aerosol from coke oven tar caused lung adenomas and squamous cell lung tumors in male mice, and squamous cell lung tumors and skin tumors in female mice. Coal tar aerosol also induced squamous cell lung carcinomas in male and female rats when administered by inhalation. Chemical analyses of coke oven emissions revealed the presence of numerous known carcinogens and potentially carcinogenic chemicals, including 5 of the 15 polycyclic aromatic hydrocarbons (PAHs) listed elsewhere in this document (see Polycyclic Aromatic Hydrocarbons, 15 Listings). Coke oven emissions also contain a variety of nitrosamines, coal tar, arsenic compounds, and benzene (see Coal Tars and Coal Tar Pitches). In addition to carcinogens, coke oven emissions contain several agents known to enhance the effect of chemical carcinogens, especially on the respiratory tract (IARC 1984, 1985).

PROPERTIES

Bituminous coals are blended and heated to 1,000 to 1,400°C in the absence of oxygen to produce coke. Tars and light oils are distilled out of the coal, and gases are generated during this process. Coke oven emissions are defined as the benzene-soluble fraction of total particulate matter generated during coke production. These emissions are complex mixtures of dusts, vapors, and gases that typically include PAHs, formaldehyde, acrolein, aliphatic aldehydes, ammonia, carbon monoxide, nitrogen oxides, phenol, cadmium, arsenic, and mercury. Air samples collected at coke plants have identified more than 60 organic compounds and more than 40 PAHs. One metric ton of coal yields approximately 545 to 635 kg of coke, 45 to 90 kg coke breeze (large coke particulates), 7 to 9 kg ammonium sulfate, 27.5 to 34 L coke-oven gas tar, 55 to 135 L ammonia liquor, and 8 to 12.5 L light oil. Approximately 20% to 35% of the initial coal charge are emitted as gases and vapors. Most of these gases and vapors are collected in by-product coke production. Coke oven gas includes hydrogen, methane, ethane, carbon monoxide, carbon dioxide, ethylene, propylene, butylene, acetylene, hydrogen sulfide, ammonia, oxygen, and nitrogen. Coke-oven gas tar includes pyridine, tar acids, naphthalene, creosote oil, and coal-tar pitch. Benzene, xylene, toluene, and solvent naphthas may be extracted from the light oil

* No separate CAS Registry Number is assigned to coke oven emissions.

fraction (IARC 1984).

USE

The primary use of coke is as a fuel reductant and support for other raw materials in iron-making blast furnaces (Kirk-Othmer 1999). Coke is also used to synthesize calcium carbide and to manufacture graphite and electrodes, and coke-oven gas is used as a fuel (IARC 1984). Coal tar, a by-product of the production of coke from coal, is used in the clinical treatment of skin disorders such as eczema, dermatitis, and psoriasis (IARC 1985). Other by-products are refined into commodity chemicals (e.g., benzene, toluene, naphthalene, sulfur, ammonium sulfate, etc.) (Kirk-Othmer 1999).

PRODUCTION

Coke production in the U.S. steadily increased between 1880 to the early 1950s, peaking at 72 million tons in 1951. In 1976, the U.S. ranked number two in the world with 52.9 million tons of coke, or about 14.4% of the world production (Kirk-Othmer 1979). By 1990, the U.S. produced 27 million tons and was ranked fourth in the world. A continuing decline in production is expected. Demand for blast furnace coke has also declined in recent years because technological improvements have reduced the coke rates by 10% to 25% (Kirk-Othmer 1999).

An estimated 330,000 to 3.5 million lb of coke oven emissions were produced annually in the U.S. (Chem. Eng. News 1984). Although, the by-product process is designed to collect the volatile materials given off during the coking process, emissions escape because of structural defects around the doors or charging lids, improper use of engineering controls, improper work practices, and insufficient engineering controls (IARC 1984).

EXPOSURE

The primary routes of potential human exposure to coke oven emissions are inhalation and dermal contact. Occupational exposure may occur during the production of coke from coal or while using coke to extract metals from their ores, to synthesize calcium carbide, or to manufacture graphite and electrodes. Workers at coking plants and coal tar production plants, as well as the residents surrounding these plants, have a high risk of possible exposure to coke oven emissions. OSHA estimated that 10,000 coke oven workers were potentially exposed to coke oven emissions annually (NIOSH 1976).

A study presenting the 1979 to 1983 measurements of exposure of employees to coke oven emissions at a steel plant found the levels among selected job classifications to be as expected given the job descriptions and the coking process (Keimig *et al.* 1986). Approximately 60% of the total emissions occur during charging, 30% during pushing, and 10% during quenching (Kirk-Othmer 1979). Larry car operators, lidmen, and door machine operators stationed very close to the oven are exposed to volatiles released from the topside and side during charging and/or coke pushing, and therefore, have the highest mean breathing zone concentrations. Intermediate in the exposure rankings are the benchman-coke side and benchman-pusher side, who are exposed to volatiles through door leakage, but are able to move away during the pushing operation. The group exposed to the lowest concentrations consists of the pusher operator, quencher car operator, heater, and heater helper; the operators do not work close to the coke ovens, while the heater and heater helper, who regulate gas reversals and check

the oven temperatures, are mainly found in the control room. Data compiled by the IARC (1984) indicated that average concentrations of coke oven emissions in the breathing zones of workers were the lowest for the pusher-machine operator (0.39 mg/m^3) and highest for lidman (3.22 mg/m^3), tar chaser (3.14 mg/m^3), and larry-car operator (3.05 mg/m^3). During the past several decades, pollution control efforts have reduced coke oven emissions (Kirk-Othmer 1979, Costantino *et al.* 1995). In a recent assessment of occupational exposure to coke oven emissions, the highest mean concentrations were reported for lidman (0.52 mg/m^3), tar chaser (0.43 mg/m^3), and larry car operator (0.19 mg/m^3) (Chen *et al.* 1999).

REGULATIONS

The Carcinogen Assessment Group at EPA has designated sludge from coking operations as a potential carcinogen, and these sludges are regulated under the hazardous waste disposal rule of the Resource Conservation and Recovery Act (RCRA). EPA has also listed components of coke oven emissions as hazardous air pollutants under the Clean Air Act (CAA). The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) designates coke oven emissions as a hazardous substance and lists a final reportable quantity (RQ) of 1 lb for coke oven emissions. NIOSH has recommended a workplace standard of 0.2 mg/m^3 as a 10-hr time-weighted average (TWA) concentration for exposure to the cyclohexane-extractable fraction of coke oven emissions.

The OSHA standard for coke oven emissions is a permissible exposure limit (PEL) of 0.15 mg/m^3 as an 8-hr TWA. Under this standard, specific engineering and work practice control requirements became effective. OSHA has also promulgated a PEL of $\leq 0.2 \text{ mg/m}^3$ as an 8-hr TWA for coal tar pitch volatiles. NIOSH and OSHA have recommended work practices to minimize the harmful effects of exposure to coke oven emissions. OSHA also regulates the coke oven emissions under the Hazard Communication Standard and as a chemical hazard in laboratories. Regulations are summarized in Volume II, Table 49.

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